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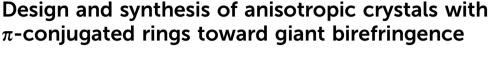
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REVIEW

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Birefringent crystals play a significant role in linear optical devices due to their ability to modulate the polarization of light. Commercial birefringent crystals MgF₂, α-BaB₂O₄, CaCO₃, YVO₄, TiO₂, and LiNbO₃ have been widely used as polarization devices in the past decades. A variety of crystals have been developed to meet the requirements of large birefringence and have great potential as optical functional crystals. However, a key question is how to balance the conflict between the energy gap and birefringence. In this review, aiming to better judge the integrated properties of optical crystals, we came up with the birefringent quality factor. We also summarised our recent findings on the birefringent crystals, which contain structural units similar to $[B_3O_6]^{3-}$ rings, from these perspectives, including crystal structure features, optical performances, and structure-property relationships. We summarised the strategy to achieve the balance between the energy gap and birefringence by adjusting the delocalized π -conjugation and the confined π -conjugation to improve the performance of birefringent crystals, which will open up a new window for the exploration of novel birefringent crystals.

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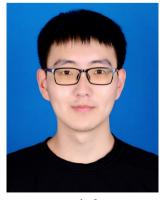
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1 Introduction

Birefringence is a linear optical property that occurs in anisotropic crystals. In anisotropic crystals, birefringence will arise when the refractive index of light changes based on the direction of light. According to the difference in optical properties,

crystals can be divided into two types, isotropic crystals and anisotropic crystals. In terms of symmetry, crystals with cubic symmetry belong to isotropic crystals. In consequence, they lack birefringence. In contrast, anisotropic crystals have more types of symmetry, including triclinic, monoclinic, orthorhombic, tetragonal, hexagonal, and trigonal symmetry. Therefore, they can generate birefringence. The crystals belonging to trigonal, hexagonal, and tetragonal systems are called uniaxial crystals, in which the unique optical axis coincides with the highest axis of symmetry. Birefringence can modulate polarized light in uniaxial crystals and spilt the incident light into ordinary ray (o) and extraordinary ray (e). They correspond to



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different refractive indices, n_0 (ordinary refractive index) and n_e (extraordinary refractive index) (Fig. 1). If $n_0 > n_e$, the crystal is called the negative uniaxial crystal. On the contrary, $n_0 < n_e$ for the positive uniaxial crystal. The birefringence can be expressed in the following equation:

$$\Delta n = |n_{\rm o} - n_{\rm e}|$$

In recent decades, several commercial birefringent crystals have been developed, including MgF₂, ² α-BaB₂O₄ (α-BBO), ^{3,4} calcite (CaCO₃),⁵ YVO₄,⁶ rutile (TiO₂)⁷ and LiNbO₃.⁸ Birefringent materials benefit to obtain phase matching in the specific wavelength range of the transparency and can be used to modulate the polarization-related light propagation. Because of these excellent optical properties, birefringent crystals are used in various optical devices, such as circulators, polarizers, phase compensators, wave plates, and optical isolators. 9-15

The properties of the compound are closely associated with the structure of the microstructure group, so it is crucial to choose suitable units. In birefringent materials, planar groups

containing π orbitals demonstrate better polarization anisotropy than the non-planar units. ^{16–19} For example, α -BBO has a large birefringence (exp. $\Delta n = 0.12 \text{@} 532 \text{ nm}$), and is transparent in the significant ultraviolet (UV) spectral region ($\lambda < 400$ nm). This is mainly attributed to the delocalized π -conjugated electron orbitals in the $[B_3O_6]^{3-}$ rings (Fig. 2). Recently, a number of birefringent crystals similar to α-BBO have been discovered, such as $K_2(HC_3N_3O_3)\cdot 2H_2O$ (exp. 0.19@514 nm),²⁵ $Rb_2(HC_3N_3O_3)$ (cal. 0.40@532 nm), ²⁶ $K_2Mg(H_2C_3N_3O_3)_4\cdot 4H_2O$ (cal. 0.38@800 nm), 27 NaRb₃(H₂C₃N₃O₃)₄·3H₂O (cal. 0.39@532 nm)²⁸ and $(C_5H_6ON)^+(H_2PO_4)^-$ (cal. 0.25@1064 nm).²⁹

In order to make devices smaller, birefringent crystals should have large birefringence. From the structural perspective, π conjugated rings are beneficial for increasing birefringence, and birefringence also depends significantly on the alignment and direction of the structural units.³⁰ The more parallel the ring, the more anisotropic is enlarged, causing larger birefringence. On the other hand, the energy gap plays a decisive role in optical crystals' applications, and thus keeping the balance of birefringence and energy gap is also a considerable problem.



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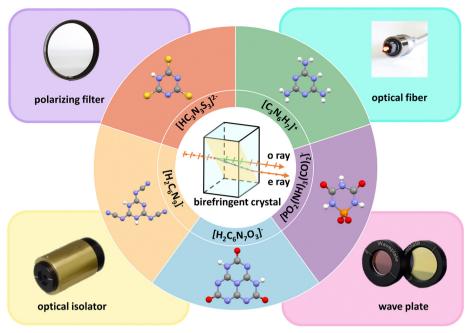
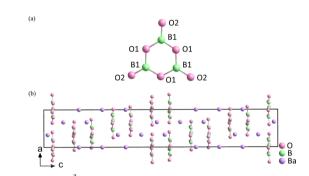


Fig. 1 The principle of birefringence, structural units, and typical applications of commercial birefringent crystals



(a) $[B_3O_6]^{3-}$ ring. (b) Crystal structure of α -BBO.

In this review, we summarised our recent efforts in exploring birefringent crystals containing π -conjugated rings. In addition, the birefringent quality factor (BQF) is used to quantify the integrated optical performance, and it can be expressed in the following equation:

$$BQF = E_g \times \Delta n$$

Table 1 Space groups and optical properties of birefringent crystals with π orbitals

Compounds	Space groups	Δn	Energy gap (eV)	BQF	Ref.
α-BaB ₂ O ₄	$R\bar{3}c$	0.12@532 nm	6.56	0.79@546 nm	20
$(C_3N_6H_7)_2SiF_6\cdot H_2O$	$P2_1/n$	0.15@550 nm	4.76	0.71@550 nm	31
$(C_3N_6H_8)PbBr_4$	$P2_1/c$	0.32@550 nm	3.13	1.00@550 nm	32
$Cs_3Cl(HC_3N_3S_3)$	$Pmc2_1$	0.52@550 nm	3.34	1.74@550 nm	33
$CsH_2C_6N_9 \cdot H_2O$	$P\bar{1}$	0.55@550 nm	4.12	2.27@550 nm	34
$Ba(H_2C_6N_7O_3)_2$	Fdd2	0.24@550 nm	4.10	0.98@550 nm	35
$8H_2O$					
$NaPO_2(NH)_3(CO)_2$	$P2_1/c$	0.28@550 nm	6.50	1.82@550 nm	36

Where E_g represents the energy gap in electron volt, Δn is the birefringence. The BQF is a valid measure of the overall performance of the material. The birefringent crystals with large BOF exhibit better integrated performance. They overcome the problem of birefringence and energy gap, where one property is large while the other is very small. As shown in Table 1, the birefringent crystals exhibit relatively large BQF, demonstrating that our design and synthesis of birefringent materials based on the α -BBO structural template is effective.

2 Structure and optical properties of birefringent crystals with π orbitals

Herein, some structures like α -BBO are summarised, including $(C_3N_6H_7)_2SiF_6\cdot H_2O_7^{31}$ MLAPbBr₄ (MLA = melamine),³² $Cs_3Cl(HC_3N_3S_3)^{33}$ $CsH_2C_6N_9\cdot H_2O^{34}$ $Ba(H_2C_6N_7O_3)_2\cdot 8H_2O^{35}$ and NaPO₂(NH)₃(CO)₂. 36 In addition, from the perspective of the fundamental structural units, the polarizability anisotropy, and the gap from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of structural units are summarised in Fig. 3. The polarizability anisotropy and HOMO-LUMO gap were calculated via the Gaussian 09 package³⁷ with the hybrid B3LYP functional at 6-31G(d,p) level. After that, the calculation results were analysed by the Multiwfn 3.8 code.³⁸ The polarizability anisotropy of all structural units exceeds that of the $[B_3O_6]^{3-}$, providing the basis for large birefringence.

(C₃N₆H₇)₂SiF₆·H₂O crystallizes in the monoclinic space group $P2_1/n$. The fundamental structural blocks contain a protonated melamine [C₃N₆H₇]⁺, [SiF₆]²⁻ octahedron, and the H_2O molecules. $(C_3N_6H_7)_2SiF_6\cdot H_2O$ combines the planar π conjugated $[C_3N_6H_7]^+$ with the highly coordinated $[SiF_6]^{2-}$ groups.

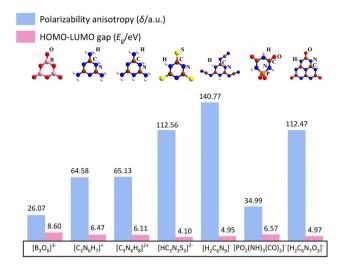


Fig. 3 Polarizability anisotropy and HOMO-LUMO gap of $[B_3O_6]^{3-}$, $[C_3N_6H_7]^+$, $[C_3N_6H_8]^{2+}$, $[HC_3N_3S_3]^{2-}$, $[H_2C_6N_9]^-$, $[PO_2(NH)_3(CO)_2]^-$, $[H_2C_6N_7O_3]^-$ anion units.

The $[SiF_6]^{2-}$ octahedra present in the gap along the c-axis connect the quasi-two-dimensional $[C_3N_6H_7]_{\infty}$ (Fig. 4a). In addition, the H₂O molecules with hydrogen bonds connect the adjacent $[SiF_6]^{2-}$ octahedra (Fig. 4b). The $[SiF_6]^{2-}$ octahedron is also connected to four [C₃N₆H₇]⁺ cations by hydrogen bonds. The parallel structure group $[C_3N_6H_7]_{\infty}$ chains lead to larger birefringence due to the π -conjugated $[C_3N_6H_7]^+$, which is similar to the $[B_3O_6]^{3-}$ functional units of α -BBO, showing high anisotropy. Inside the single $[C_3N_6H_7]_{\infty}$ chain, adjacent $[C_3N_6H_7]^+$ cations are further linked by two N-H...N hydrogen bonds, resulting in the coplanar alignment (Fig. 4c). In addition, the highly symmetrical [SiF₆]²⁻ polyhedron further facilitates the aligned arrangement of each [C₃N₆H₇]_∞ chain. The Kubelka-Munk function $F(R) = (1 - R)^2/2R$ is used to calculate the absorption rate of light, where R is the reflectance.³⁹ Additionally, the experimental energy gap can be inferred by extrapolating the linear part of the rising curve to zero. The large energy gap is 4.76 eV (Fig. 4d), suggesting the (C₃N₆H₇)₂SiF₆·H₂O

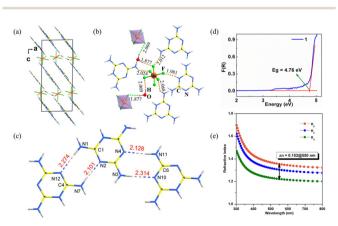


Fig. 4 (a) Structure of $(C_3N_6H_7)_2SiF_6\cdot H_2O$ viewed along the *b*-axis. (b) The coordination environment of $[SiF_6]^{2-}$ octahedra. (c) $[C_3N_6H_7]_{\infty}$ chain formed by hydrogen bonds. (d) Absorption spectra. (e) Theoretically calculated refractive indices and birefringence of (C₃N₆H₇)₂SiF₆·H₂O.³¹

crystal can be used in the UV region. The birefringence of $(C_3N_6H_7)_2SiF_6\cdot H_2O$ is 0.15@550 nm (Fig. 4e). Thus, the BQF is 0.71@550 nm. In accordance with the crystal structure and theoretical calculation, the birefringence and energy gap of (C₃N₆H₇)₂SiF₆· H₂O should be due to the parallel aligned protonated melamine $[C_3N_6H_7]^+$ groups and the highly symmetric $[SiF_6]^{2-}$ octahedron.

The MLAPbBr4 crystallizes in the centrosymmetric monoclinic space group of $P2_1/c$. The crystal structure of MLAPbBr₄ is composed of melamine cations [C₃N₆H₈]²⁺ (Fig. 5a) and PbBr₆ octahedra (Fig. 5b). The structure combines the corrugated $[PbBr_4]_{\infty}$ layers with the melamine cations to form a (110)oriented perovskite framework (Fig. 5c). According to the absorption data, the energy gap of MLAPbBr₄ is about 3.13 eV, meaning the optically transparent window can achieve to the UV spectral region of 374 nm. In addition, the experimental birefringence (0.32@550 nm) was calculated according to the formula $R = \Delta n \times$ T. 40,41 Where R represents the optical path difference, T represents the thickness of the crystal, and Δn represents the birefringence. Hence, the BQF is 1.00@550 nm. The first-principles calculation is used to explore the potential mechanism of the large birefringence of MLAPbBr₄. As shown in Fig. 5d, theoretical birefringence is 0.29@550 nm, which is in agreement with the experimental value. The HOMO and LUMO of MLAPbBr4 were calculated to show the origin of birefringence. Through Fig. 5e, for highly π -conjugated melamine cations, the HOMO shows an apparent anisotropy of electron densities, and the LUMO reflects highly distorted PbBr₆ octahedra. Hence, the delocalized π -conjugated melamine cations and distorted PbBr₆ octahedra coordinate to enlarge the birefringence of MLAPbBr₄.

Cs₃Cl(HC₃N₃S₃) crystallizes in the non-centrosymmetric space group of Pmc2₁. The crystal structure of Cs₃Cl(HC₃N₃S₃) is composed of [HC₃N₃S₃]²⁻ rings (Fig. 6a), which is similar to the α -BBO, and ClCs₆ polyhedra (Fig. 6b). According to the Fig. 6c, the chains are parallel along the a axis, with the coplanar [HC₃N₃S₃]²⁻ rings occupy the interchain space. According to the UV-visible-near-infrared diffuse reflectance spectrum of Cs₃Cl(HC₃N₃S₃) powders, the absorption edge is

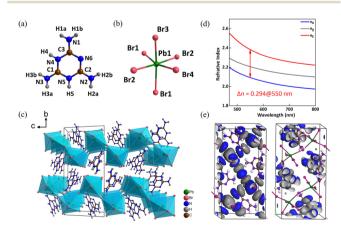


Fig. 5 (a) Crystal structure of melamine cation. (b) Crystal structure of PbBr₆ octahedron. (c) Viewed along the a-axis, the crystal structure of MLAPbBr₄. (d) Theoretically calculated refractive indices and birefringence of MLAPbBr₄. (e) HOMO and LUMO of MLAPbBr₄. 32 Copyright 2022, Wiley.

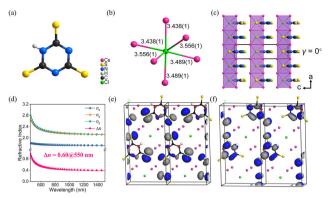


Fig. 6 (a) $[HC_3N_3S_3]^{2^-}$ ring. (b) $ClCs_6$ polyhedron. (c) The crystal structure of $Cs_3Cl(HC_3N_3S_3)$, (γ) is the dihedral angle between the $[HC_3N_3S_3]^{2^-}$ rings and the (100) plane. (d) Theoretically calculated refractive indices and birefringence of $Cs_3Cl(HC_3N_3S_3)$. (e) The HOMO of $Cs_3Cl(HC_3N_3S_3)$. (f) The LUMO of $Cs_3Cl(HC_3N_3S_3)$. (Black, red, green, yellow, purple and white balls represent C, N, Cl, S, Cs and H atoms, respectively). ³³ Copyright 2022, Wiley.

near 371 nm with a corresponding energy gap of about 3.34 eV. The measured birefringence of Cs₃Cl(HC₃N₃S₃) is 0.52@550 nm. Thus, the BQF is 1.74@550 nm. To reveal the underlying mechanism of birefringence, first-principles calculations were calculated. As shown in Fig. 6d, the calculated Δn of Cs₃Cl(HC₃N₃S₃) is 0.60@550 nm, which is close to the measured birefringence. The HOMO and LUMO for crystal Cs3Cl(HC3N3S3) reflect the origin of birefringence (Fig. 6e and f). The HOMO is composed of the N 2p orbitals and S 3p orbitals, and the LUMO is mainly constituted by the π orbitals on the $[C_3N_3]$ rings and the 3p orbitals of the S atoms. Therefore, from the perspective of structure-property relationships, the [HC₃N₃S₃]²⁻ structural unit is crucial to the birefringence of Cs₃Cl(HC₃N₃S₃) because of the delocalized π -conjugation. In addition, the $[HC_3N_3S_3]^{2-}$ rings are parallel to the (100) plane, which enlarge the anisotropic. It makes a positive contribution to improving birefringence.

CsH₂C₆N₉·H₂O crystallizes in the centrosymmetric space group of triclinic P1. As the fundamental structural unit of CsH₂C₆N₉·H₂O, the [H₂C₆N₉] unit is made up of the three almost coplanar linear -(N-C≡N)- side arms and the planar π -conjugated [C₃N₃] ring (Fig. 7a). In addition, consistent with the reported protonated tricyanomelaminates, the H atoms in the [H₂C₆N₉] unit are bonded to the N atoms of the [C₃N₃] rings. 42-44 As shown in Fig. 7b, CsH2C6N9·H2O has a pseudotwo-dimensional layered structure with Cs⁺ counter cations present in the interlayer space to maintain the overall charge balance. The [H₂C₆N₉]⁻ anion units are held in place by the hydrogen bonding network, which belongs to the nearly coplanar H₂O molecules. The coplanarity of [H₂C₆N₉]⁻ anion units is an optimal arrangement for optical anisotropy and is conducive to the generation of large birefringence in CsH₂C₆N₉·H₂O, similar to the cases in α -BBO. ⁴⁵ According to the UV-visible-near-infrared diffuse reflectance spectrum, CsH₂C₆N₉·H₂O has an absorption edge at about 301 nm in the UV spectral region. This represents an experimental energy gap of about 4.12 eV. The experimental birefringence of CsH₂C₆N₉·H₂O (0.55@550 nm) was measured

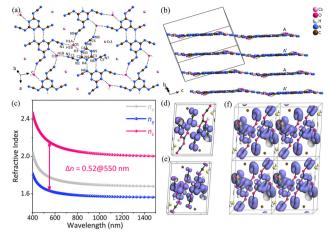


Fig. 7 (a) $[H_4C_6N_9O]_{\infty}$ single layer in $CsH_2C_6N_9 \cdot H_2O$. (b) The pseudotwo-dimensional layered structure of $CsH_2C_6N_9 \cdot H_2O$. (c) Theoretically calculated refractive indices and birefringence of $CsH_2C_6N_9 \cdot H_2O$. (d) The HOMO of $CsH_2C_6N_9 \cdot H_2O$. (e) The LUMO of $CsH_2C_6N_9 \cdot H_2O$. (f) π orbitals of $(H_2C_6N_9)^-$ in $CsH_2C_6N_9 \cdot H_2O$, the fuchsia, yellow, brown, dark green and white spheres represent N, O, Cs, C and H atoms respectively. 34 Copyright 2022, Wiley.

using a polarizing microscope. 46 Hence, the BQF is 2.27@550 nm. The first-principles calculations were used to explore the microscopic origin of birefringence. According to the relationship between the wavelength and refractive index, the birefringence of CsH₂C₆N₉·H₂O is 0.52@550 nm, which agrees well with the measurement. In addition, there is a large anisotropy of refractive indices in CsH₂C₆N₉·H₂O (Fig. 7c). As shown in Fig. 7, the electron localization function (ELF)^{47,48} maps of CsH₂C₆N₉·H₂O have been presented, aiming to illustrate the contribution of Cs⁺, H₂O molecules, and [H₂C₆N₉]⁻ units. In Fig. 7d, the HOMO consists mainly of N 2p orbitals. In addition, N 2p and C 2p orbitals of $[H_2C_6N_9]^-$ predominate the LUMO (Fig. 7e). Especially, the π orbitals of the linear –(N–C \equiv N)– in the $[H_2C_6N_9]^$ and [C3N3] rings are parallel to one another and also parallel to the π orbitals in the adjacent $[H_2C_6N_9]^-$ (Fig. 7f). Such a structural arrangement enhances microscopic anisotropy, thus increasing the birefringence. Therefore, the large birefringence of CsH₂C₆N₉·H₂O can be attributed to the delocalized π -conjugated orbitals in the $[H_2C_6N_9]^-$ units.

Ba(H₂C₆N₇O₃)₂·8H₂O crystallizes in the non-centro-symmetric orthorhombic of the *Fdd*2 space group. The crystal structure of Ba(H₂C₆N₇O₃)₂·8H₂O consists of an independent [H₂C₆N₇O₃]⁻ anion (Fig. 8a), one Ba²⁺ cation, and four lattice H₂O molecules. In Fig. 8c, Ba(H₂C₆N₇O₃)₂·8H₂O exhibits a three-dimensional framework composed of π-conjugated [H₂C₆N₇O₃]⁻ anions, Ba²⁺ cations, and H₂O molecules. In Ba(H₂C₆N₇O₃)₂·6H₂O, each Ba²⁺ cation is shared by six H₂O molecules and two [H₂C₆N₇O₃]⁻ anions *via* Ba–O bonds. The UV-visible-near-infrared diffuse reflectance spectrum of Ba(H₂C₆N₇O₃)₂·8H₂O ranges from 200 nm to 1000 nm, the UV absorption edge of Ba(H₂C₆N₇O₃)₂·8H₂O is situated at λ = 302 nm, which corresponds to an energy gap of 4.10 eV. The measured birefringence of Ba(H₂C₆N₇O₃)₂·8H₂O is 0.24@ 550 nm. The theoretical value of birefringence is 0.22@550 nm,

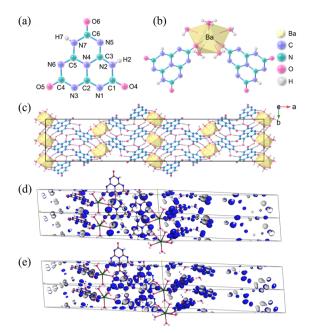


Fig. 8 (a) The $(H_2C_6N_7O_3)^-$ anion. (b) The coordination environment of Ba²⁺. (c) Viewed along the crystallographic c-axis, the crystal structure of $Ba(H_2C_6N_7O_3)_2 \cdot 8H_2O$, and the yellow polyhedra represent BaO_8 polyhedra. (d) The HOMO of $Ba(H_2C_6N_7O_3)_2 \cdot 8H_2O$. (e) The LUMO of Ba(H₂C₆N₇O₃)₂·8H₂O.³⁵ Copyright 2022, Wiley

which agrees well with the experimental value. Hence, according to the energy gap and measured birefringence, the value of BQF is 0.98@550 nm. To investigate the cause of the large birefringence, the HOMO and LUMO patterns of Ba(H₂C₆N₇O₃)₂·8H₂O are shown in Fig. 8d and Fig. 8e. O 2p and N 2p orbitals are the main constituents of the HOMO. In comparison, the unoccupied π orbitals make up the LUMO components. In summary, due to the expanded π -conjugated

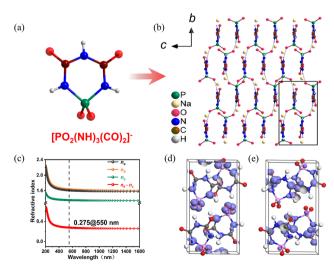


Fig. 9 (a) $[PO_2(NH)_3(CO)_2]^-$ anion. (b) Along the a-axis, the crystal structure of NaPO2(NH)3(CO)2. (c) Theoretically calculated refractive indices and birefringence of $NaPO_2(NH)_3(CO)_2$. (d) The HOMO of $NaPO_2(NH)_3(CO)_2$. (e) The LUMO of NaPO₂(NH)₃(CO)₂. ³⁶ Copyright 2022, Elsevier.

delocalization in the [H₂C₆N₇O₃]⁻ building blocks, it has an enhanced birefringence.

NaPO₂(NH)₃(CO)₂ crystallizes in the monoclinic space group $P2_1/c$. As shown in Fig. 9a, the crystal structure of NaPO₂(NH)₃-(CO)₂ consists of six-membered rings [PO₂(NH)₃(CO)₂] formed by direct covalent bonding of two π -conjugated planar triangles $[CO(NH)_2]$ and a non- π -conjugated tetrahedron $[PO_2N_2]$. The $[PO_2(NH)_3(CO)_2]^-$ anions form a bond with the Na⁺ cations present in the vacancies (Fig. 9b). The UV-visible-near-infrared diffuse reflectance spectrum indicates that the energy gap is 6.50 eV. In addition, the experiment birefringence is 0.28@ 550 nm. Thus, the value of BQF is 1.82@550 nm. To investigate the fundamental relationship between optical performance and structure of NaPO₂(NH)₃(CO)₂, first-principles calculations were used. In Fig. 9c, NaPO₂(NH)₃(CO)₂ has a calculated birefringence of 0.28@550 nm and exhibits pronounced optical anisotropy, in general agreement with the measured value. The HOMO and LUMO were calculated to investigate further the relationship between optical properties and crystal structure at the molecular level (Fig. 9d and e). It demonstrates that the π -conjugated interactions have been partially decoupled by the $PO_2(NH)_2$ tetrahedron, and all of the π -conjugation is confined within the [PO₂(NH)₃(CO)₂]⁻ ring. Hence, in order to keep an effective balance between a large energy gap and large birefringence, the confined π -conjugation of $[PO_2(NH)_3(CO)_2]^-$ units play a crucial role, and the integrated properties of the birefringent crystal are improved.

3 Conclusion

In this review, we have presented and discussed systematically the recent development of π -conjugated birefringent materials. We discussed the crystal structure, energy gap, birefringence, and the relationship between structure and property. For the birefringent materials containing π -conjugated groups, here are some perspectives and outlooks.

- (1) The delocalized π -conjugated C-N rings show strong hybridization between C and N atoms and contribute significantly to the birefringence of crystals. In addition, in order to achieve an effective balance between the large energy gap and the large birefringence, confined π -conjugation plays a critical role. Confined π -conjugation can partially decouple the π -conjugated interaction, and compared with the delocalized π -conjugation, confined π -conjugated birefringent crystals have a larger energy gap. At the same time, birefringent crystals with confined π -conjugation can maintain a suitable birefringence. Since birefringence and energy gap are important factors in the application of birefringent crystals, a reasonable balance between delocalized π -conjugation and confined π -conjugation is essential to improve the integrated performance of birefringent crystals.
- (2) In addition, the birefringence depends significantly on the anisotropy of the structure, while the anisotropic structure depends on the arrangement of the unit. Therefore, the internal arrangement of the structural unit should be considered.

An effective strategy to enhance birefringence is to induce an ordered arrangement of the π -conjugated unit.

- (3) This paper reviews the synthesis of several large BQF crystals. According to the structure–property relationship, the optical properties of birefringent crystals depend on the microscopic groups and the arrangement of the groups within the crystal. Exploring suitable microscopic groups with large polarizability anisotropy and HOMO–LUMO gap and controlling their ordered arrangement increased the BQF of the birefringent crystals.
- (4) Perovskite and anti-perovskite are novel structural systems in the development of birefringent crystals. They can increase the anisotropy and thus the birefringence through the optimal arrangement of cations. This is also an important direction in the study of birefringent crystals.
- (5) The structure containing H_2O will reduce the stability of the crystal. One way to improve the stability of crystals is to replace the H_2O molecule with the halogen atom.
- (6) With the continuous improvement in computing power and the development of theoretical calculation theory, bottom-up synthesis strategies can also be applied to the design and synthesis of birefringent crystals. The microscopic hyperpolarizability, polarizability anisotropy, and HOMO–LUMO gap can be calculated to select suitable groups, and then the different functional units can complement each other to form highly integrated birefringent crystals. This is also useful in the design and synthesis of novel birefringent crystals.

Conflicts of interest

There are no conflicts to declare.

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